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Characterization of Trace Metal Associations with
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Characterization of Trace Metal Associations with Polluted Marine Sediments by Selective Extractions

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KEY WORDS: trace metals, sediments, selective extraction, ferric oxides, manganese oxides

Sediments are a major sink for trace metals in the marine environment and consequently can also act as a source of metals to overlying water when the environmental conditions to which the sediments are exposed are altered [1]. As part of an effort to assess the hazards to the aquatic environment associated with marine disposal of dredged material, the U.S. Environmental Protection Agency and the U.S. Army Corp Of Engineers have been involved in a joint Field Verification Project (FVP). One research component of the FVP is the chemical characterization of the dredged material, including the determination of identities and levels of contaminants in marine organisms, thus presenting a threat to the environment. In evaluating the impact of marine disposal of dredged material, the form in which metals are incorporated into particulate matter is of great significance to both the environmental effects and fate of those metals.

Marine sedimentary particulate matter consists of many different components and phases, including crystalline minerals, carbonates, hydrous metal oxides, and organic substances. Metals may be associated with particulate matter by a number of mechanisms, such as ion exchange, coprecipitation, complexation with organic substances, incorporation into mineral lattices, and so forth. The effects of geochemical processes on sedimentary metals are strongly

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dependent on the forms in which the metals are present. Specific affinities of metals for different particulate phases can vary by orders of magnitude between different metals and types of particles or particle surface coatings. The empirical determination of affinities of metals for different particulate surfaces and knowledge of sediment components enables development of predictive models for partitioning of metals in the sediments and estimation of the important species of some metals under a given set of conditions [2].

Metals present in different chemical forms in sediments would also be expected to have differing availabilities to marine organisms; metals adsorbed to or bound within an organic or hydrous oxide coating, for example, are more biologically available than metals incorporated with crystalline mineral lattices. Biological uptake of an element varies between different solid phases and assimilation from a given phase varies between metals [3]. Assimilation of metals was found to increase with decreasing sediment-metal binding strength (indicated by the partitioning coefficient). The nature of the associations between metals and sediments can also change as sediments undergo alterations through environmental interactions. Thus the biological availability of sediment-bound metals can also change over a period of time.

The diversity of particulate matter composition makes a complete division of individual metal-particle interactions impossible. A more practical approach is the separation of particulate matter-metal associations into operationally defined classifications based on the nature and reactivity of the reagent(s) necessary to extract the metal from the particulate matter. A number of selective extraction procedures have been developed to characterize the nature of binding between metals and aquatic particulate matter [4-10]. Selective extractions can simulate different environmental conditions, which can influence the fate of particulate metals and predict the effects resulting from alterations of the sediments' environment, such as occurs in dredging and disposal of sediments. Extraction procedures have been applied to studies of metal-particle associations in a variety of aquatic environments [4, 10-16]. These studies have demonstrated the importance of iron and manganese oxide coatings and organic matter in binding of metals to marine particulates and the variety of association mechanisms involved with sediments from varying sources.

The Field Verification Project has intended to assess the potential effects and hazards involved with marine disposal of dredged sediments. This work seeks to enhance that effort by characterizing the nature of the trace metal-particulate matter associations in material dredged from Black Rock Harbor and determining whether environmental alterations in those associations have taken place during or after disposal of the material in central Long Island Sound.

Experimental Procedure

Sample Collection

Figure 1 illustrates the locations of Black Rock Harbor, CT, where the harbor channel dredging took place and the disposal and reference sediment sites in Central Long Island Sound (CLIS). Twenty-five bottom sediment samples from Black Rock Harbor were collected before dredging by the U.S. Army Corps of Engineers using a 0.1-m² box corer. The sediments were combined, homogenized, and stored in clean barrels for subsequent chemical and physical analysis [17]. Individual barrels of dredged sediments used for characterization studies were rehomogenized by sieving through a 1-mm-stainless steel screen and extensive hand stirring with plastic paddles in a fiberglass tank. Aliquots of the sediments were stored in 1-L brown glass and 250-mL polyethylene containers at 4°C until analysis. Metals analyses were performed on several samples from each barrel to ensure chemical homogeneity within and between dredged material.

Disposal of 55 000 m³ of Black Rock Harbor dredged material took place in the CLIS disposal area in May 1983. Sediment samples from stations around the disposal area were col-

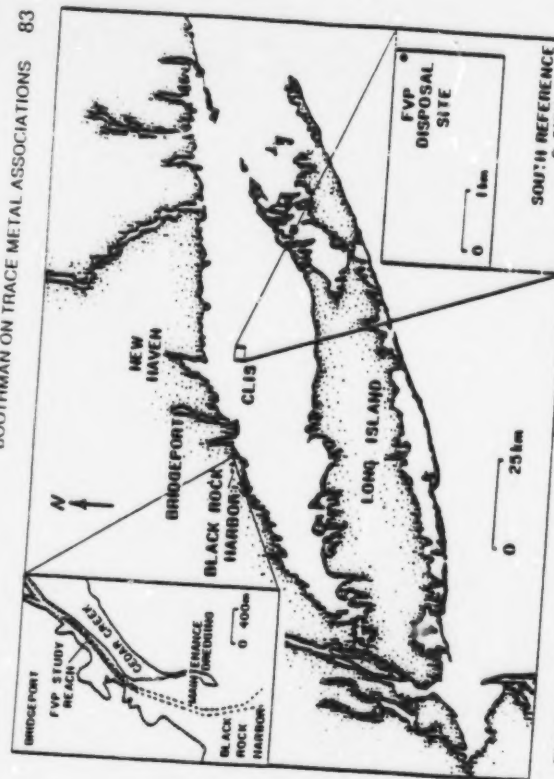


FIG. 1—Locations of Black Rock Harbor dredging operation and Central Long Island Sound disposal site.

lected with a 0.1-m² Smith-MacIntyre grab sampler. Sediment cores 10 to 15 cm deep were taken from the grabs using acrylic tubes with polyethylene end caps. The cores were frozen until sectioning, when each core was partially thawed and sliced into 2-cm-thick sections using a stainless steel spatula. The individual sections were completely thawed and homogenized by hand before subsampling for metals extraction and analysis.

Sample Preparation and Analysis

Triplicate specimens, approximately 1 g in weight, of each sample (either dredge material or CLIS sediment) were weighed wet into acid-leached 30-mL polysulfone Oak Ridge type centrifuge tubes for extraction. Sediments were characterized using the sequential extraction method of Hong [10]. Five millilitres of extraction solution was added to each of the wet sediment specimens, the centrifuge tubes were capped, and the specimens extracted according to the conditions listed in Table 1. Four fractions of particulate matter were defined by the extractions performed: exchangeable (EX), weak acid soluble (WA), oxidizable (OX), and strong acid soluble (SA).

The exchangeable and weak acid soluble extractions were performed with ultrasonic agitation at room temperature. For the oxidizable and strong acid soluble extractions, the centrifuge tubes were placed in graphite heating blocks and heated to 90°C. After each extraction, the specimens were centrifuged, the supernatant removed, and 5 mL of deionized water (18 000 mΩ-cm resistivity) added as a wash to the residual specimen in the centrifuge. The specimens were agitated 15 min ultrasonically and centrifuged again. The wash solution was combined with the extractant solution, stored in a 20-mL acid-leached polyethylene vial and the next extractant added. The same sequence was followed for all four fractions in the sequence. Because

TABLE 1—Selective extractions of particulate phases.

Fraction	Extraction	Particulate Phases Extracted
Exchangeable	1.0 N $MgCl_2$, overnight, 25°C	dissolved interstitial, weakly surface-bound metals
Weak Acid	pH 4 acetate buffer overnight, 25°C	Fe and Mn hydrous oxides, carbonates
Oxidizable	30% H_2O_2 , pH 2, 1 h, 90°C	sulfides, organic matter
Strong acid	concentrated HNO_3 , 1 h, 90°C	residual nonmineral material

the interstitial water in any specimen was not separated before addition of the first extraction, the exchangeable fraction contains both dissolved and weakly surface-bound metals. Reagent/procedural blanks were run along with the specimens for all fractions.

Separate triplicate specimens were weighed into 7-mL polypropylene vials for freeze-drying. The specimens were reweighed after freeze-drying to determine the moisture content of each sample. The mean value was used to normalize each extracted sediment concentration to a dry weight basis.

The extracted solutions were analyzed for copper, chromium, lead, and cadmium using flame and heated graphite furnace atomic absorption spectrophotometry on a Perkin-Elmer Model 5000 spectrophotometer equipped with a Model 500 graphite furnace and utilizing Zeeman effect background correction. Absorbance data were collected on a Perkin-Elmer 3600 data station. Specimen concentrations were calculated from calibration curves determined by aqueous standards and confirmed by standard additions. Extraction solution concentrations were combined with the mass and volume data for the specimen to calculate metal concentrations on a dry weight basis. Total extracted concentrations for each metal were calculated as the sum of the concentrations in the individual fractions, and the distribution among the operational fractions determined as the percentage of the total metal determined in a sample present in each fraction.

All specimen preparation and analytical data were processed and stored in data bases on a PDP 11/70 computer using the DATMAN data management system.

Results and Discussion

Characterization of Metal-Particulate Matter Associations in Black Rock Harbor Dredge Material

Table 2 presents some of the physical characteristics of the Black Rock Harbor (BRH) dredge material. As is typical of dredged sediments, water content and the fraction of fines are both

TABLE 2—Physical characteristics of BRH dredge material.

Characteristic	Value
Grain size	86 to 95% fines
% Water	69.0 ± 7.0
% TOC	5.63 ± 0.15
pH	7.3
COD	highly reduced

very high. As a result, BRH is a material very easily dispersed in the water column, and upon disposal in CLIS is spread in a mound several 100 m in diameter. The pH of the material is not substantially different from that of the environment into which the material is disposed; however, its highly reduced state, evidenced by the heavily sulfurous odor evolved upon opening any of the barrels, can be significantly affected by, and have an effect upon, the estuarine environment.

The distributions of cadmium, copper, chromium, and lead among operationally defined fractions in BRH and in core samples taken from the center of the disposal mound (CNTR) in late July 1983, about two months after the disposal, are presented in Figs. 2 through 5. The bars in the figures represent the mean percentage of the total metal in the sample found in each fraction. The error bars represent one standard deviation for each percentage; the numbers above each set of bars give the mean and standard deviation of the total concentration of the metal determined in that sample.

As might be expected from the highly reduced state of the dredged material, most of the metals analyzed in BRH are found predominantly in the oxidizable fraction, that is, associated with organic matter and sulfides; in the cases of cadmium and copper, greater than 90% of the total metal is in the oxidizable fraction. Only lead has a distribution not dominated by association with oxidizable particulate matter, with almost 80% found in the residual, strong acid soluble fraction. By comparison, sediments from the reference site (not shown) appear to be more highly oxidized. The oxidizable fraction in reference site sediments contains a much smaller percentage of the total metals than in BRH, while the strong acid soluble fraction is much larger, comprising 70 to 100% of the metals in surface sediments and 40 to 60% of the total metals in subsurface sediments (except for lead, where it comprises 96 to 98%).

Variations of Metal-Particulate Distributions with Sediment Depth

Variations of the cadmium sediment phase distributions with depth (Fig. 2) in a core from the CNTR station collected 26 July 1983, about two months after the disposal, are indicative of significant changes, particularly in the surface sediment. The total cadmium concentration in the uppermost section (0 to 2 cm) is only one-fourth of the concentration in the dredge material and increases with depth over the first 8 cm, then decreases in the last (8 to 10 cm) section. The actual dredged sediments were not as well-mixed as the barrel samples and contain varying proportions of sediment fines, which would be dispersed to a greater extent than coarse, sandy portions. Since a large fraction of the metals would be expected to be associated with the fine sediment [18], the variation in total cadmium concentration may reflect differing extents of dilution of the metal with sand rather than chemical alteration of the dredged material during or after disposal.

The distribution of cadmium among the selectively extracted sediment phases clearly indicates a substantial change, however. The exchangeable fraction contains about 20% of the total cadmium in the surface section, with an additional 20% in the weak acid soluble fraction. In BRH these fractions each comprised less than 5% of the total. While the major portion of the cadmium found in the surface sediment is still associated with oxidizable particulate matter, that fraction represents only about 60% of the total, about 30 percentage points less than the dredge material. In addition to increasing total cadmium concentrations, the cadmium distribution increasingly resembles that of the dredged material as the depth of sediment increases. The subsurface sediments have smaller exchangeable and weak acid soluble fractions and concomitantly larger oxidizable fractions, although even in the 8 to 10-cm section the weak acid soluble fraction is significantly larger than in the dredge material.

As pointed out previously, the highly reduced condition of the dredged material is likely to be significantly altered by the more oxidizing environment at the CLIS disposal site. Both organic matter in the dredged material and sulfides formed under anoxic sediment conditions may be oxidized, altering the binding of metals to those materials. The formation of oxides of iron and

Particulate Cd sediment phase distribution
CNTR, 26 JULY 83

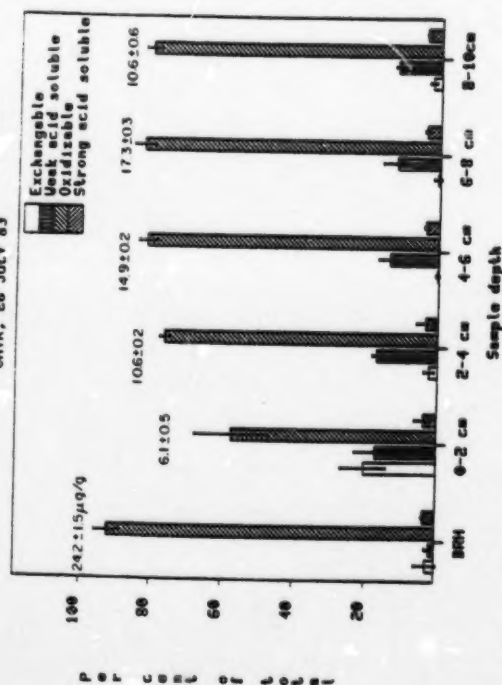


FIG. 2—Cadmium particulate phase distribution in BRH and variation with depth in CLIS sediments at center of mound.

manganese, which are present in high concentrations in the sediments, will also affect the nature of association of metals with the sediments. Both of these factors (organics and sulfides, iron, and manganese oxides) play significant roles in controlling the distribution of metals between dissolved and particulate phases in aquatic systems [19]. The increased proportion of cadmium in the exchangeable and weak acid soluble fractions, particularly in surface sediments, appears likely to be the result of oxidation of reduced matter and iron and manganese in the dredge material, altering the interaction between the metal and sediment particles.

The distribution of copper (Fig. 3) is similar to that of cadmium. Copper is primarily associated with oxidizable particulate matter in BRH (greater than 95% of the total) and total concentrations determined in the CLIS sediments increase with depth in the core. In contrast to the cadmium distribution, though, there is no significant change in the particulate phase distribution with depth for copper, except for a very slight increase in the exchangeable fraction in the 0- to 2-cm sample. This suggests that the variations in total metal concentrations in the sediments are indeed a result of differing relative amounts of sand in the samples, but that the particulate phase distributions reflect the results of chemical effects. The differences between the cadmium and copper distributions can have at least two explanations.

Copper and cadmium may be associated with different oxidizable components of the sediment. Copper is known to bind strongly to organic substances, and may be primarily associated with sediment humic substances. Cadmium, on the other hand, forms highly insoluble sulfides and could be present in the dredge material mostly in that form. Both metals would then be found in the oxidizable fraction. The environment in the sediments may be sufficiently oxidizing to convert sulfides to soluble sulfates, but not enough so to oxidize humic substances in the sediments. In such a case, the cadmium associated with the sulfides would be predominantly solubilized, but copper would remain associated with the oxidizable fraction in the sediment.

Particulate Cu sediment phase distribution
CNTR, 26 JULY 83

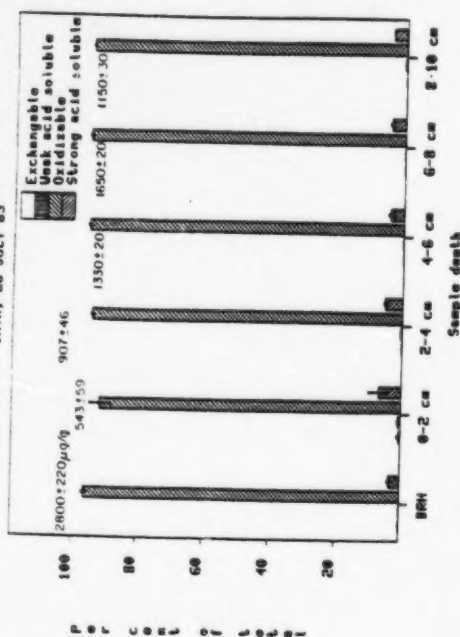


FIG. 3—Copper particulate phase distribution in BRH and variation with depth in CLIS sediments at center of mound.

It is also possible that copper and cadmium may be associated with the same components in the dredged sediments, but may establish different equilibria when placed in the marine environment. For example, cadmium forms very strong chloride complexes; relatively high chloride concentrations in marine waters may compete with organic material for cadmium and stabilize the metal as soluble complexes. Since copper chlorocomplexes are not as stable, the marine chloride would not compete as well with organic substances for copper ions and most of the copper would still be associated with the oxidizable fraction of the sediment.

The sediment core profiles for chromium and lead (Figs. 4 and 5) are similar to copper; the sediment distributions are very similar to the distributions determined in the dredge material, and little or no change with depth in the distributions for either metal is observed. The lack of variation in the sediment distributions implies that no significant geochemical alteration has taken place in the association of these metals with the sediment particulate matter, at least within the two months following disposal when this core was sampled.

Variations of Metal-Particulate Distributions with Time

Further illustration of the geochemical alterations of the metal-particulate associations in CLIS surface sediments is given by Figs. 6 through 9. Total concentrations determined vary by a factor of ten or more. This variability is a result of several factors: (1) sediment heterogeneity in the mound makes variability large, even between samples from the same date; (2) sampling procedures and conditions cause variability in the actual location of the sampling; and (3) currents and biological activity can physically redistribute sediments. Nonetheless variations in the particulate phase distributions of metals in the sediments indicate changes in the chemical nature of associations between trace metals and the sediments.

The most striking example is given by the variation in the cadmium distributions (Fig. 6).

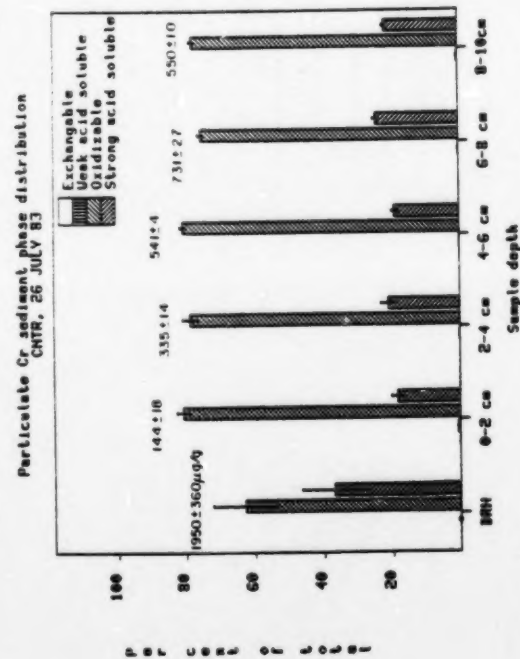


FIG. 4—Chromium particulate phase distribution in BRH and variation with depth in CLIN sediments at center of mound.

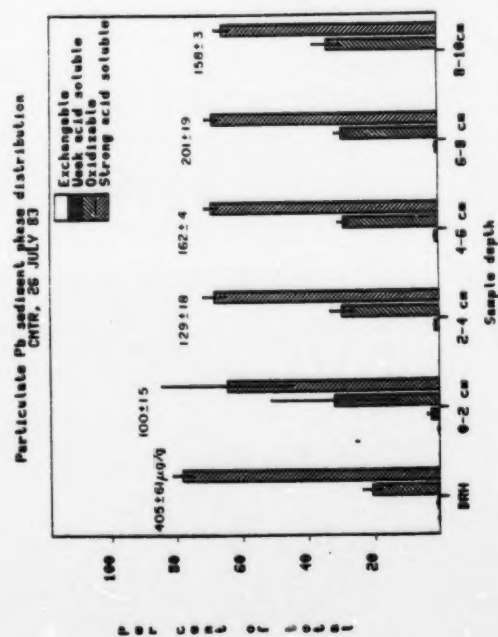


FIG. 5—Lead particulate phase distribution in BRH and variation with depth in CLIN sediments at center of mound.

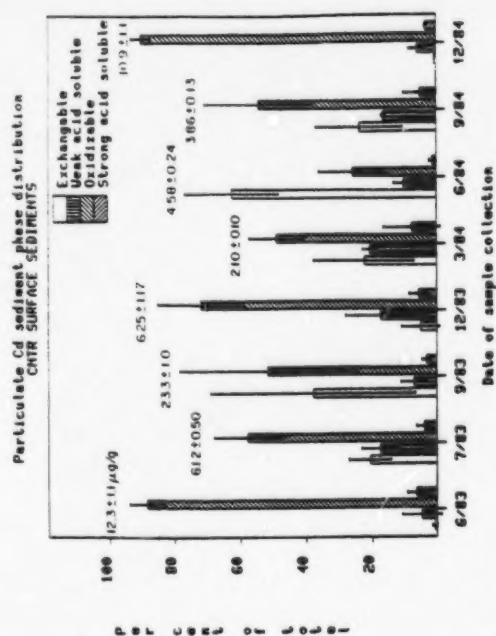


FIG. 6—Variation of cadmium particulate phase distribution with time in CNTR surface sediments.

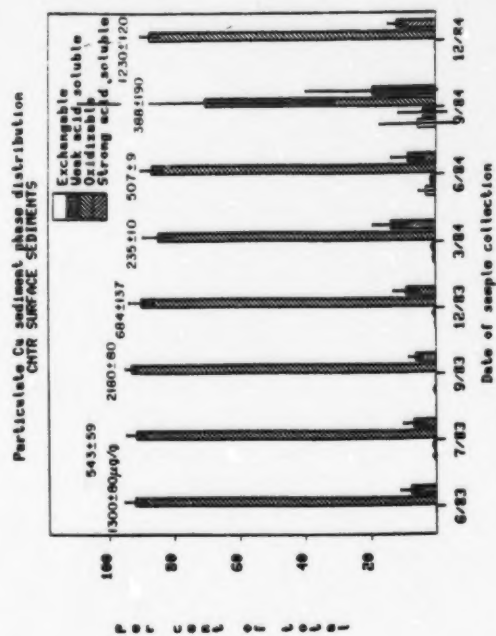


FIG. 7—Variation of copper particulate phase distribution with time in CNTR surface sediments.

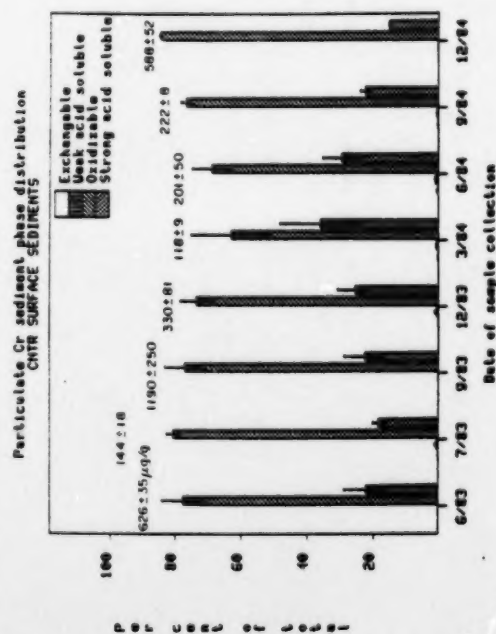


FIG. 8—Variation of Chromium particulate phase distribution with time in CNTR surface sediments.

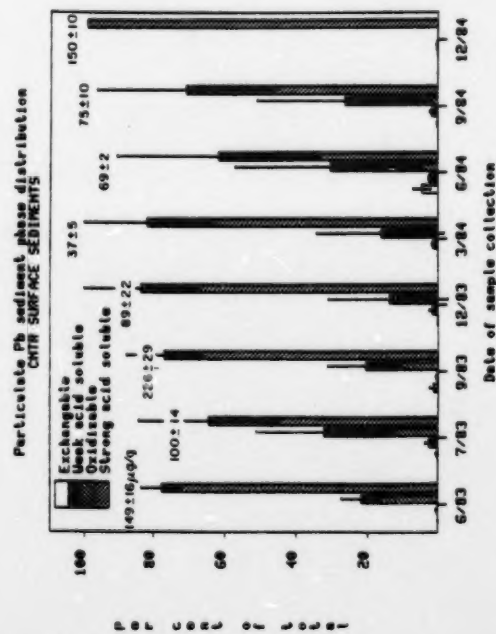


FIG. 9—Variation of lead particulate phase distribution with time in CNTR surface sediments.

The distribution found in CNTR surface sediments in early June 1983 is very similar to that in the dredge material before disposal (BRH, Fig. 1). Greater than 90% of the cadmium is presently associated with oxidizable particulate matter, indicating that very little alteration of the dredge material took place during the disposal operation. The distributions determined in July and Sept. 1983, however, show a marked increase in the proportion of the exchangeable and weak acid soluble fractions. The Dec. 1983 distribution is similar to that of BRH acid samples from March, June, and Sept. 1984 again have significant exchangeable and weak acid soluble fractions. The increase of the more weakly bound fractions in the warmer months suggests a seasonal process (or processes) altering the metal-sediment interaction. For example, oxidation of organic matter and sulfides in the sediments. Limitations on *in situ* processes could be due to water temperature, biological activity, or possibly other seasonal variables. The decreased proportion of cadmium in the exchangeable and weak acid soluble fractions in the winter months is more likely to be caused by increased turbulence in the water column caused by winter weather removing the oxidized surface sediment and exposing relatively unaltered subsurface sediments rather than reduction reactions in the sediment.

The sediment phase distribution of copper in CNTR surface sediments (Fig. 7) initially shows very little variation from that found in the dredged material. In spring and summer of 1984, however, the exchangeable and weak acid soluble fractions show a distinct increase. While the increase in these fractions is much lower for copper than for cadmium, the process responsible for the increase (that is, oxidation of the sediments) could be expected to be the same. Again association with differing components of the oxidizable fraction of the sediments or differences between copper and cadmium in equilibria could lead to the differing extents of alteration.

As in the distributions seen in the sediment core samples, the surface sediment phase distributions for chromium (Fig. 8) and lead (Fig. 9) show almost no variation over the time period sampled. Slight increases in the exchangeable and weak acid soluble fractions of lead may be seen in samples collected during the summers of 1983 and 1984. The increases are very small and could represent input of new material to the surface sediments rather than alterations in the lead already present. The lack of any substantial variation in the sediment phase distributions implies that no significant alteration is taking place in the sediment binding of chromium and lead.

Conclusions

In the current study, cadmium, copper, and chromium present in dredged material from an industrialized harbor were found to be associated predominantly with oxidizable particulate matter. Lead, on the other hand, was found almost entirely in the strong acid soluble fraction of the dredged material. Because of anoxic conditions in the dredged material, sulfides must be considered at least as significant as organic matter in the composition of this oxidizable material. Alteration of these oxidizable components in a more oxidizing environment, resulting in modification of associations of copper, cadmium, and chromium and the dredge material, can readily be expected. Lead, however, can be expected to be relatively inert to changes in the sediment environment.

Characterization of the metal-particulate associations in sediments from the center of the CLIS disposal site have confirmed alterations in the sediments. The sediment phase distributions of cadmium and, to a lesser extent, copper have evidenced an apparent seasonal oxidation of surface sediments and redistribution of the cadmium and copper to exchangeable and weak acid soluble (that is, hydrous oxide) sediment phases. Oxidation apparently occurred over a period of time in the sediments rather than the disposal of the material. As expected from the phase distribution of lead in the Black Rock Harbor dredged material, little evidence of change in the interaction of lead with sediment particulate matter is observed. Chromium also demonstrates no significant change in particulate matter associations, despite its predominant associ-

ation with the oxidizable fraction in the dredged material. The reason for the lack of geochemical activity of chromium is not clear at present.

The redistribution of metals in sediments to more labile phases has potentially significant implications with regard to availability of metals to benthic organisms and remobilization of metals from sediments to the water column. Characterization of the distribution of metals in sediments may enable prediction of the uptake of metals from polluted sediments by organisms. Furthermore the increase in dissolved and weakly bound metals in surface sediments may represent a means of remobilization of sediments metals. Seawater data for dissolved and particulate cadmium and other metals at the disposal site during the time period of this study are being compiled to test this possibility.

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